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Next 4 Page(s) In Document Denied

Violent Reaction in Polymerization Processes at Low

Temperatures and in Polymers with Conjugated Bands

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The author will devote the first part of the lecture to the kinetics of polymerization and to the reactions of free radicals at relatively low temperatures.

There are still only a few experimental studies in this field, however during recent years the interest of scholars has been increasing rapidly in this direction.

Clearest of all is the manifestation of a violent, almost explosive polymerization at the moment of fusion of a solid monomer, which was already observed in the forties by Letort<sup>1</sup>, Hinshelwood<sup>2</sup>, Norrish<sup>3</sup>, and in recent times by Enikolopian (Institute for Chemical Physics), in the case of acetaldehyde. The reaction takes place with the speed of the fusion process without using catalysts, whereas a trifle above or a trifle below the fusion temperature there is practically no reaction.

The same phenomenon as shown by Enikolopian is also observed at the melting point of formaldehyde. There are many indications in the literature on this subject of violent polymerization reactions at the melting point and for other monomers at a low temperature (e. g. styrene and methyl methacrylate). When the melting temperature of substances is higher than 0°, this phenomenon is either not observed or is

-2-

observed in the form of a slight speed increase. Abkin reports, for instance, that the latter takes place when melting maleic anhydride (56°).

Kargin, Kabanov and others<sup>4</sup> deposited on a glass surface, chilled by means of liquid nitrogen, a monomer and a catalyst in the form of two molecular films in a vacuum. At a certain temperature of the precipitate there occurred an explosive polymerization reaction. Monomers tested were: methyl methacrylate, styrene, acetone, acrylo- and methacrylonitril, acrylamide, isoprene, and others. As catalysts: magnesium, lithium, mercury, chlorides of lithium or beryllium, Mo O<sub>3</sub> and others were used. It was discovered that styrene, isoprene and  $\alpha$ -methylstyrene react violently upon fusion. Other monomers (in particular, formaldehyde) display a violent, often explosive polymerization at markedly lower temperatures, obviously, upon transition of the precipitate from an amorphous to a crystalline state. Above or below this critical temperature the reaction takes place extremely slowly. Similar phenomena were observed by Magat<sup>5</sup> upon irradiation of formaldehyde at a temperature of about -196°.

It is also interesting that a rapid reaction is observed during the fusion of a mixture of components not only during polymerization, but also during other simpler reactions.

In the Department of Chemical Kinetics of Moscow State University, Chaikin<sup>6</sup>, Vishnevskii and Sergeev<sup>7</sup> a few years ago observed violent reactions of chlorination and hydrochlorination when freezing a mixture of chlorine with ethylene or isobutylene and correspondingly with hydrogen chloride.

-3-

Semyonov and Shalnikov<sup>8</sup> back in the twenties, while directing molecular films of sulfur and cadmium onto a surface cooled by liquid air, observed under the same experimental conditions as Kargin and Kabanov an explosive reaction when attaining a certain critical temperature below -100°.

In the Department of Chemical Kinetics of Moscow State University, Gurman and his associates<sup>56</sup> observed at -115° a violent reaction for the recombining of free radicals in a frozen 25 percent solution of  $H_2O_2$  in  $H_2O$ . The radicals were obtained at -196° by exposure to ultraviolet light and were registered by the EPR method. At temperatures above or below -115° the radicals were stable during a prolonged time. In the absence of illumination the system  $H_2O_2$  (25 percent) +  $H_2O$  (75 percent) at precisely -115° displays on a thermographic curve a phase transition. Thus, the reconstruction of the lattice, or the transition from an amorphous to a crystalline state, furthers a rather rapid movement of the radicals, which also provides for a great recombination speed.

Let us also remember that the mixtures of pulverized oxides of alkali and alkaline-earth metals with oxides and chlorides of elements of the IVth Group at temperatures considerably lower than the melting temperature react at the points of polymorphous transformation of one of the components with the formation of complex compounds. This phenomenon was investigated in an especially detailed manner by Urazov and his students. As was shown by Evdokimov<sup>57</sup> at the Institute of General and Inorganic Chemistry, such a process takes place

-4-

also when the chloride is in a vapor phase. He studied the system consisting of one or another oxide of an alkaline-earth metal and of a germanium tetrachloride vapor. For different oxides, the temperature of polymorphous transformation (and the accompanying reaction) is between 200 and 640°, while the melting temperature of oxides is of the order of 2000°. This observation shows that at the time of the phase transition the oxides became permeable to the molecules of vapors.

Furthermore, the author will examine several peculiarities of polymerization at low temperatures in the liquid phase upon initiation by means of penetrating radiation, light, and catalysts. It has long been known, particularly from industrial experiments, that the polymerization speed of liquid isobutylene under the action of acid catalysts increases with the lowering of the temperature.

Under the action of gamma rays, isobutylene is also polymerized at low temperatures (e.g. at -80°), with a much greater speed than at 0°. Here, under low temperature conditions there is formed a polymer of high molecular weight, while at the usual temperature (e.g. at 0°) low molecular products are formed. The speed of radiation-polymerization of liquid isobutylene and of its solutions in electron-acceptor solvents is strictly proportional to the intensity of the gamma rays, which is an indication of an ionic mechanism for the process.

Abkin<sup>9</sup> showed that the polymerization speed of acrylonitrile in a solution increases (approximately 17 times) when the temperature is lowered from -50 to -112°; also the molecular weight of the polymer obtained greatly increases.

-5-

As is known, at positive temperatures, the speed of this reaction decreases when the temperature is lowered. Thus, the speed of the polymerization reaction that takes place in the solution has a minimum and increases in the direction of high and low temperatures. Abkin links this with the transition from a radical mechanism, that is characteristic for high temperatures, to an ionic mechanism, that is characteristic for low temperatures.

Enikolopian at the Institute of Chemical Physics studied the polymerization of isobutylene in a liquid state under the action of penetrating radiation in the temperature interval from -20 to -120°. The reaction speed increases when the temperature is lowered (about 16 times in the interval indicated), obeying the law of Arrhenius, but as though with negative activation energy  $E = -2.47$  Kcal/mole. The speed of radiation-polymerization was strictly proportional to the intensity of radiation. The speed of polymerization is equal to  $IP$ , where  $P$  is the average rate of polymerization, and where  $I$  is the speed of production of active centers, proportional to the radiation intensity, which of course does not depend on the temperature. Unfortunately,  $P$  as a function of the temperature was not measured, but there is every reason to assume that  $P$  increases when the temperature is lowered.

Later the author will survey the polymerization of liquid methyl methacrylate. It is known that in 1958, Goode, Fox, and others<sup>10</sup> showed that at low temperature, there is formed from ~~a~~ methyl methacrylate in a liquid phase under the action

in light in the presence of peroxide, a syndiotactic polymer, while at ordinary temperatures under the same conditions an atactic polymer is obtained. Obviously the reaction proceeds according to a radical mechanism. Thus, a stereo-regular polymer was obtained for the first time in a homogeneous environment. Enikolopian investigated the kinetics of the low temperature polymerization of methyl methacrylate in the temperature interval from 25 to -48° under the same conditions as in the work of Goode and others, i.e., with the initiation of the process by means of free radicals. It was shown in particular, that the absorption of light by peroxide in the investigated temperature interval was constant. The same was done for vinyl acetate. The polymerization speed is proportionate to  $\sqrt{I}$ .

The time of the development of the chain was determined by the method of a rotating sector, the reaction speed by the dilatometric method, and the polymerization rate by the viscometrical method. The constant for the growth of the chain  $k_g$  was calculated by ordinary equations. For the polymerization at temperatures above 0°,  $k_g$  and the activation energy corresponding to these values coincided with the data of other authors (Melville and others). However, when the temperature was lowered, the law of Arrhenius is not observed (Figure 1). The effective activation energy decreases when the temperature is lowered. The values of constants observed at low temperatures are noticeably greater (about 3 times) than those which would be obtained for these low temperatures (-48°) by means of extrapolating, according to the law of

-7-

Arrhenius, those data obtained at higher temperatures. The experimental curve shown in Fig. 1 cannot, it appears, be obtained in presupposing a binomial formula for the constant of the growth of the chain

$$k_p = k_{synd} + k_{isotact} = A_1 e^{-E_1/RT} + A_2 e^{-E_2/RT}$$

As Enikolopian showed, the function obtained by him obviously cannot be explained from the generally accepted viewpoint which consists of the following: that the polymerization process (no matter whether radical or ionic) consists of a series of elementary acts, in each of which is added one molecule of a monomer.

Enikolopian through the rotating sector method determined the time  $\tau$  of development of the chain during low temperature polymerization of an illuminated methyl methacrylate, to which was admixed a peroxide. According to the usual theory, the time  $\tau$  is determined by the speed of initiation and the speed of destruction of the chain. It was not dependent on the temperature (in other words, the recombination constant of the radicals does not depend on the temperature). The time  $\tau_c$  between two consecutive acts of juncture to polymerized radicals of two molecules of a monomer must be equal to

$$\tau_c = \frac{1}{k_p[M]} .$$

Thence the kinetic length of the chain, i.e. the number of elementary acts in the chain

$$v = \frac{\tau}{\tau_c} = k_p[M] \tau .$$

-3-

When there is no transmission of the chain (which for the polymerization of methyl methacrylate was firmly demonstrated by Melville<sup>11</sup>), the usual theory leads to the equation  $\gamma = \bar{P}$  (with a break by means of disproportionation) and  $\bar{P} = 2\gamma$  (with a break as a result of recombination). However, from an experiment Enikolopian obtained  $\bar{P} = \gamma$  only at temperatures higher than 0, but when the temperature was lowered the ratio  $\bar{P}/\gamma$  increases, reaching 6.5 at -48°.

Below the author endeavors to give another type of mechanism for the reaction of the chain increase at lowered temperatures.

Let us examine the work in radiation-polymerization in a solid monomer.

During the last years there appeared a series of works (Mesrobian, Bamford, Magat, Moravets, Ballantine and others<sup>2</sup>) on the study of polymerization in a solid phase under the action of irradiation at low temperatures. As Magat showed, the polymerization speed under the action of radiation exposure in a solid phase is usually 10 - 15 times greater than in the liquid phase, even if the temperature in the solid phase is lower.

In many cases of radiation-polymerization in solid monomers, there is observed a so-called post-effect, i.e. a prolonged reaction process after the exposure to radiation has been discontinued. This <sup>phenomenon</sup> manifestation was studied in particular detail by Moravets<sup>13</sup> in the <sup>case</sup> instance of polymerization for a crystalline acrylamide at a temperature of 25°. In this case

the post-effect lasts for days. In 100 hours the depth of transformation reaches altogether 20 percent. Moravets considers this post-effect a result of the extremely slowed down reaction process of chain increase, and the significant reaction speeds during constant exposure to radiation a result of an even greater decrease of the chain destruction constant ( $k_d$ ). When compared with Dainton's data<sup>14</sup>, the former is according to Moravets  $10^5$  less than in an acrylamide solution at the same temperature, and the latter  $10^9$  times less. The constants  $k_g$  and  $k_d$  were obtained by Moravets by comparing experimental data of how the transformation depth of polymerization depended on the time with the theoretical curve obtained from ordinary kinetic polymerization equations.

We must, however, keep in mind that Dainton and Tordoff, when studying the polymerization of acrylamides in solution, also observed a strong post-effect which lasted many hours with a slowly decreasing speed. However, this post-effect, as they showed, is not directly proportional to the magnitude of the chain growth constant. The time of development of the chain was determined by Dainton by the rotating sector method during the process of stationary reaction (during irradiation) and was equal in all to about 30 seconds. Therefore, Dainton considers that the post-effect is linked to the temporary break of the chain, or with the screening of the free radical, or,--and this he considers more plausible--it takes place at the expense of the conversion of a polymerization-active radical into a non-active form with free valence at the nitrogen

-10-

atom. Both in the first and the second case under the action of thermal motion the activity of a radical may be again restored (in the second case as a result of the reverse transition of the radical to an active form). In these cases the small chain after a prolonged damping again begins to increase quite rapidly either by continuation of this chain, or by creating a new one. Inasmuch as the processes of the conversion of active forms of the radical into non-active ones take place very slowly in comparison with the speed of chain development up to its temporary damping, it is natural that the post-effect will continue for a long time.

The author presupposes that in solid acrylamide during its polymerization the post-effect has an analogous nature.

The considerable speed of radiation-polymerization reaction in solid polymers, numerous authors (e.g. Moravets) link with their crystalline structure. Frequently the supposition is expressed that the relative disposition of monomers in a crystal is close to the orientation of reacting molecules most favorable for the chain growth reaction. Thus, in the report presented to this symposium, Bensasson and Marx<sup>15</sup> say that the decrease of activation energy chain growth occurs because of the favorable orientation of monomer molecules in a crystal. Let us observe that such a type of favorable orientation of a radical and a monomer should not by itself cause a lowering of activation energy in a solid versus its value in the liquid phase. In the latter case, as in the gaseous phase with an activation energy of 4 - 5 Kcal, only

these particles react that are by chance favorably orientated upon collision. The orientation in a crystal may only influence the magnitude of the pre-exponential term. This consideration is overlooked by many authors. The authors express the hypothesis that such a favorable orientation in a crystal enables the polymeric ion or radical to annex at once not one neighboring molecule of a monomer, but the entire chain of molecules in the region where the crystal is ideal. This question is discussed in detail below, but now we examine the phenomenon of energy transfer at low temperatures.

Let's turn to the experimental facts. For the sake of definiteness and brevity we may consider only the work conducted along these lines in recent years at the Institute of Chemical Physics, in the laboratories of Talroze, Voyevodskii and Buben, and at the Institute of Petrochemical Synthesis in the laboratory of Polak. Talroze and Frankevich<sup>16</sup> studied the electrical properties of polyethylene and paraffin which arise when heating samples previously irradiated in the solid state. The irradiation took place at the temperature of liquid nitrogen with fast (1.5 mev.) electrons, and also with hard X-rays. Simultaneously, the spectra of the electronic paramagnetic resonance (EPR) of the free radicals were fixed. The free radicals in these systems are stable at low temperatures and only when heated to a certain temperature do they begin to perish rather quickly as a result of recombination. In the case of paraffin they are alkyl radicals which perish mainly at temperatures from -33 to -13°. In the case of polyethylene (as was shown especially clearly by Voyevodskii and

-15-

Buben<sup>17</sup>), these are alkyl and allyl radicals. The first ones perish in the interval from -3 to +27°, the latter in the interval from +70 to 90°. Measuring in a parallel fashion the electrical conductivity, Talroze and Frankevich discovered an outburst of electrical conductivity at the same or somewhat higher temperatures, at which a recombining of radicals occurs. During this outburst the electrical conductivity of the irradiated substance in comparison with an analogous index for a non-irradiated substance increases to the 2nd or 3rd order. This phenomenon may be furthered by the fact that a local emission of energy as a result of the recombination of a pair of radicals is able to cast out an electron ("hole") into the conduction zone.

This supposition acquires a special significance in connection with the new experiments of Talroze and Frankevich<sup>18</sup>. They discovered analogous outbursts of electrical conductivity by heating a polymer of triethylenglycoldimethacrylate, containing radicals which remain in its mass after polymerization (temperature 25°). In this case the appearance of an EMP was also observed, the magnitude of which attained several volts, which obviously bears witness to the great lengths of free run of electrons ("holes") in this system along some collective levels.

Certain new data also were obtained concerning the migration of excitation energy along the saturated hydrocarbon chain.

Voyevodskii and Buben with their associates<sup>19</sup> exposed the following <sup>to</sup> fast electrons: (1) Saturated hydrocarbons, (2) Benzene, (3) Saturated compounds in which one or two

-13-

hydrogens at the end of the molecular chain were replaced by phenyl radicals. The alkyl chain consisted of 11  $\text{CH}_2$  groups. In saturated chains, as was known, secondary alkyl radicals appeared with irradiation. In benzene, phenyl radicals are formed, the radiation yield of which is 20 - 30 times less than in the case of saturated hydrocarbon. Thus in both cases the radicals appear as a result of a breaking away of the H atoms. It was discovered that as a result of irradiation of substituted benzenes practically only radicals of the phenyl type were formed, but with a radiation yield 2 - 3 times larger than in pure benzene, calculated on the basis of direct action. These data prove the possibility of energy migration along the saturated hydrocarbon chain toward the benzene rings.

Talroze and Gusynin<sup>20</sup> studied the damping action of carbinols ( $\text{C}_1 - \text{C}_9$ ) on the luminescence of dioxane solutions, activated by terphenyl. The effectiveness of the damping action of the alcohol molecule was shown to grow linearly with the length of its hydrocarbon chain. If the effectiveness of damping were determined by the collision of excited dioxane molecules with the OH group itself, then all alcohols (in the case of identical molar concentrations) would have an identical damping effectiveness. The linear law discovered shows that the damping occurs upon the collision of an excited dioxane molecule with any part of an alcohol molecule. On the other hand, it turned out that the corresponding hydrocarbons (in which, of course, the OH group is absent)

action. These experiments directly prove the possibility of distant energy migration along the saturated hydrocarbon chain toward the OH group of the alcohol.

As another example of extremely distant energy transfer may serve the experiments of Kolbanovskii, Polak and Shcherbakova<sup>21</sup>, conducted at the Institute of Petrochemical Synthesis of the Academy of Sciences, USSR, in which the following was shown: upon irradiation of frozen heptane (at -196°) with additions of excitation acceptors such as aromatic compounds in a concentration of  $10^{-2}$  to  $10^{-4}$  moles/liter, the output of radiolysis products decreases, and the energy transfer radius may be estimated at about 100 Å.

These results coincide with the data of Porter and associates<sup>58</sup>, who studied energy transfer in an environment of methylcyclohexane + isopentane. Upon irradiation with gamma rays in the presence of about  $10^{-3}$  moles of triphenylmethane, the authors discovered an increased yield of triphenylmethane radicals on account of energy transfer from the solvent. Since, however, in Porter's work the radiolysis products of the environment were not measured, the work of Polak and associates is a more direct proof of the transfer of energy in these systems. From Porter's data the transfer radius may be estimated at about 60 Å, which is close to Polak's data.

The ability of molecules to concentrate the energy of ionizing radiations increases of course substantially with

-15-

the increase of conjugation. Barkalov, Berlin, Goldanskii and Dzantiev in the Institute of Chemical Physics studied the radiation-polymerization of phenylacetylene in solutions of ethyl acetate and nonane. As is known, in ethyl acetate one observes especially precisely the proportionality between the yield of the polymer (in the case of a given common dose) and the concentration of the monomer. However, in the case of the polymerization of phenylacetylene it turned out that in both named solvents the output of the polymer (for small conversion percentages) practically does not depend on the concentration of a monomer in the solution, if this concentration exceeds 5 - 10 percent. The yield of the polymer also remains the same in a monomer system without solvent. All this points to a practically complete transfer of energy, absorbed by the solvent, to the monomer and the polymeric radicals. Obviously, this is linked with the presence of an unusually strong conjugation in this polymer. The substitution of aromatic substituents on cyclohexyl rings or fatty chains significantly decreases the effect as a result of the fact that the conjugation is preserved in this case only in the basic polymeric chain.

Experimental data on the peculiarities of the polymerization reaction taking place at low temperatures can hardly be explained with the aid of the usual theory, developed for higher temperatures. There are still too few new data from which to form a theory for the phenomenon which interests the author. Not at all claiming the forming of such a theory,

the author endeavors below to present a working hypothesis which for the time being is purely qualitative.

The author supposes that in a monomer crystal the radical is able to annex all at once a group, consisting of a considerable number of monomer molecules. In line with other authors, Semyonov supposes that in a crystal the monomer molecules are disposed in a relative orientation favorable to a polymerization reaction. In a crystal there is, one might say, a "store" for the production of macromolecules, which is not found in a homogeneous liquid and which insures a faster polymerization reaction under the action of radiation for a solid monomer than for a liquid. The explosive transition process from monomeric state to a polymeric one in a solid at a certain low temperature (much below the melting temperature), observed by Kargin, Kabanov, and others<sup>4</sup>, for a series of monomers and by Magat<sup>5</sup> for formaldehyde, very much recalls the regroupings which occur just as violently in solid solutions of metals under strong supercooling. A classical example of this is the martensite regrouping in steel, where the gamma-form instantly (non-diffusely) goes over into the alpha-phase.

Since the composition and alternation of C atoms do not change on polymerization, in this case a non-diffused regrouping is possible also. However, the difference consists in the fact that during polymerization the process is linked to the change of valence bonds, i.e. to a sharp regrouping of

-17-

the electron density between the atoms<sup>C</sup> ¶.

(a) Besides, as was shown above, the regrouping in a mixture of metal oxides or of oxides with metal chlorides leads to a chemical reaction with resulting complex compounds, which, probably, is linked with the regrouping of electron density.

Therefore, it would seem that in the case of polymerization the process must have a considerable activation energy. Each addition of one monomer molecule to the radical should be connected with the same activation energy ( $\sim 5$  Kcal/mole) as in the liquid phase. The presence of a "store" would be able to strongly increase the pre-exponential term of the reaction rate constant, but not to decrease the activation energy. Meanwhile the activation energy for the polymerization reaction in a solid monomer is considerably lower than in a liquid monomer at ordinary temperatures.

We must, however, keep in mind that in the presence of a "store" there are formed exclusively favorable conditions for the transfer of energy, which is evolved in the elementary act of annexation of one molecule of the monomer (probably in the form of energy of an excited electron). This energy goes into the activation of the neighboring molecule of the monomer and consequently insures the occurrence of a subsequent elementary act without any thermal activation etc. Thus, the entire monomeric "store" from  $n$  molecules during the time necessary for the transfer of atoms of C ( $\sim 10^{-13}$  sec.) is almost instantly transferred with the aid of such energetic <sup>an</sup> <sub>reaction</sub> chain into a polymeric chain. Only when encountering a lattice defect, where the favorable disposition of molecules is upset,

-18-

does the reaction of chain growth stop. Let us observe that a violent explosive character of polymerization was observed for a series of solid monomers only at melting temperature and at a certain considerably lower temperature, which, possibly, is not precisely fixed. Kargin, Kabanov and others link this temperature with a non-equilibrium transition from a vitreous state of a monomer to a crystalline one.

In the remaining region of temperatures in a solid crystalline monomer there takes place a slow reaction of polymerization, but nevertheless, as a rule, 10 - 15 times faster than in a liquid monomer at low temperatures.

This slow process of radiation-polymerization of a solid monomer at a low temperature may be presented in the following manner.

Under the action of radiation in a crystal there are formed primary radicals as a result of the breaking off of an ~~dis~~<sup>b</sup> H atom at such a point in a molecule where it is most weakly linked. Probably, it is most favorable to break off an H atom from molecules located in the places of lattice defects. These primary radicals P are little capable of reaction as a result of the fact that their free valence is unfavorably oriented in relation to the double bond of monomer molecules in the crystal, and thereby the reduced speed of the radiation polymerization process is explained<sup>b</sup>. Nevertheless, rarely

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(b) From quantum mechanical calculations, it is known that for a reaction, e.g.  $D + H-H \rightarrow D-H + H$ , the process takes place with little activation energy only in the favorable case when three atoms lie practically on one straight line; in the case of perpendicular orientation the activation energy will be considerable.

-19-

does the interaction of a radical with a monomer molecule occur along a double bond. In this connection there is formed a secondary radical  $P-C=C-$ , whose free valence is already favorably oriented for further polymerization. The energy evolved in this reaction goes into the excitation of an electron in a neighboring molecule, etc., as a result of which there occurs practically an instantaneous formation of a polymeric chain with a free valence at the end.

Thus the process will take place as though by leaps and bounds with prolonged pauses in between. Therein the author sees particularly the explanation of the phenomenon of the post-effect, and also of the often observed gradual increase in the speed of polymerization at the beginning of stationary irradiation of a solid monomer. The chain (reaction) finally dies as a result of rare cases of recombining of end valences of two chains (bimolecular process).

If the polymerization mechanism is ionic, then under the action of radiation there are formed ion pairs of opposite charges usually in the defect points of a lattice. The direct recombination of an ion pair is very much hindered by steric reasons. There also rather rarely occurs a neutralization by means of an overbalancing onto this primary-ion pair of an electron (onto the plus ion) and of a "hole" (onto the minus ion) from a monomeric collective system. The energy evolved here, just as in the case studied above of radical polymerization, insures a simultaneous act of polymerization at once of  $n$  molecules of a crystal. The number  $n$  is again determined

by lattice defects. The electron and the "hole", existing in the last act of the development of the chain, pass onto the defect, as a result of which there arises at the end of the chain a new stable ion pair. The final cessation of the chain reaction takes place as a result of rare cases of direct recombination of a stable ion-pair (monomolecular process). There is a post-effect if the reaction of chain production takes place more rapidly than the direct recombination, and the post-effect does not take place in the reverse relation.

At melting temperature or a little higher or lower than it, the correct disposition of monomeric molecules, characteristic for a crystal, is preserved; but the molecule acquires a certain mobility, which reminds us of the mobility of molecules in a liquid, although it is not fully equivalent thereto. This facilitates the reaction of the primary radical (or of the ion-pair) with the nearest monomeric molecule, as it permits the primary radical to quickly realize the orientation favorable for the reaction.

After this act there immediately follows a practically instantaneous polymerization reaction of the entire "crystallite", since the defects may no longer delay the development of the chain.

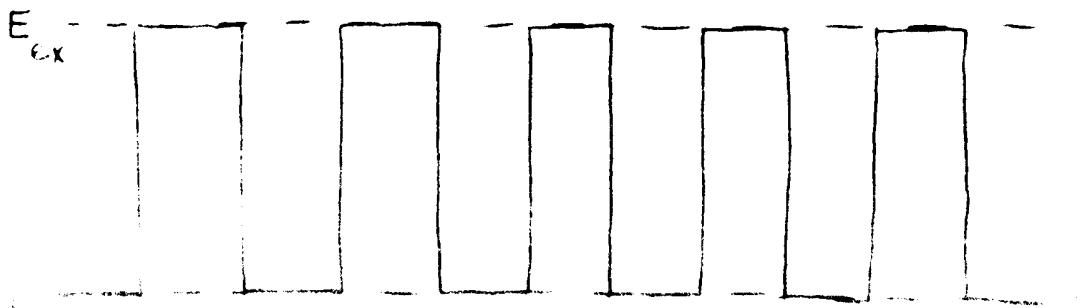
A situation similar to this also unfolds at the point of transformation of a vitreous monomer into a crystalline one or generally at the points of phase transition. In both cases there are thus created conditions for a quick, explosive type of polymerization.

-21-

During the development of the above-mentioned energetic chain, the transfer of energy evolved in the given act of the reaction adjacent to the monomeric molecule may be realized in the form of an electronic excitation.

The presence of excitation energy leads almost instantly to a reaction of annexing the monomeric molecule to the polymeric radical according to the type of photochemical processes. The activation barrier is overcome at the expense of the excitation energy as a predissociation type of phenomenon. The energy evolved in the reaction is again transferred as the excitation of the following molecule of a monomer, and the chain grows. The qualitative evaluation made by Adirovich upon the author's request proves that the boundary between the polymeric and monomeric parts of the chain must move with a speed of the order of  $10^5$  cm/sec. Thus, the chain of 1000 links will be formed during  $\sim 10^{-10}$  sec.

Thus we can draw the following picture of the energy state of an electron in the process of the rapid growth of a chain. The electron now is in an excited state with energy  $E_{ex}$  (after one reaction), then in a normal level (at the moment following the reaction) (see diagram).



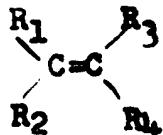
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The author expresses a supposition which it is still impossible to prove exactly. In the regular cell of a crystal the excited level is collectivized and is also the level of the excited crystal as a whole. The electron may move freely with the speed of an electron wave along the entire crystal. Besides, the author supposes that the basic level of the monomeric crystal is also collectivized to a considerable degree and this is why.

Indubitably, such a collectivization of the basic level of  $\pi$ -electrons takes place in conjugated systems. But the correct sequence<sup>c</sup>  $C=C$   $C=C$  ...  $C=C$ , which occurs for a

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(c) For brevity we use  $C=C$  instead of




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monomeric crystal, is analogous to a conjugate system. In a monomeric crystal, it is true, there are no single bonds between molecules  $C=C$ . But the possibility of sufficiently frequent sub-barrier transitions of electrons and of "holes" in monomeric crystals is not at all excluded, although the distance between the C atoms of two molecules is even greater than the distances between those inside the molecule. But this leads to a certain collectivization of  $\pi$ -electrons in the basic state of a monomeric crystal. But then there arises a natural question as to whether for each elementary reaction of the chain there is required each time a jump of

400

the electron to energy level  $E_{ex}$ , its subsequent decrease to a normal state, and then a new rise to the same level  $E_{ex}$ , etc. It is not sufficient that one electron remain at this collective level for a truly simultaneous polymerization process all at once for all  $n$  molecules of a monomer. Thus the energy evolved in the first act of joining to the primary radical, of one molecule of a monomer, goes into the excitation of a monomeric system of  $n$  molecules. After this there occurs all at once a coordinated act of the transformation of all  $n$  molecules of the monomer into a polymeric chain. This process will take place according to a type of predissociation in complex molecules.

The author tries with one example from ordinary kinetics to substantiate the supposition about the simultaneous act of transition of  $n$  molecules of a crystalline monomer to a polymer. In essence, here we suppose a simultaneous coordinated movement of nuclei, and a redistribution of electron density along the entire collective assembly of  $n$  molecules. It is well known that the break-off of the H atom from the allyl radical requires an expense of energy  $q$ , in accordance with the equation



But this means that the transposition of electron density and the transposition of hydrocarbon atoms takes place simultaneously, in one act, with a break-off of the H atom.

If the reaction took place gradually:



then the energy of the breaking-off for the H atom would be  $Q_1$ , i.e. much greater than the actually observed magnitude  $Q_1 - Q_2 = q$ .

It is much more difficult to explain on the basis of this hypothesis the peculiarities of polymerization for liquid monomers and their solutions at lowered temperatures. These peculiarities consist in the fact that, when the temperature was lowered, the speed in the liquid phase either increases or decreases more slowly than would follow from extrapolating toward the low temperatures the magnitudes of the constant  $k_g = A e^{-E/RT}$  for the chain growth; these values are characteristic for room- and higher temperatures. The apparent activation energy decreases either at the expense of the real decrease of E, or at the expense of an increase of the pre-exponential term A. If in the liquid there were formed groups (complexes) of correctly oriented (similarly to a crystal) molecules and the free radical could, when encountering this complex, annex immediately these  $n$  molecules, then the peculiarities of polymerization in a liquid phase at low temperatures could be explained on the basis of the hypothesis introduced above.

Unfortunately it is difficult to substantiate the emergence of such complexes, since the van der Waals forces are

-25-

weak. Besides, even if such complexes were formed, then in a homogeneous liquid or in solutions their number would change very little with the lowering of the temperature. The question arises whether there are not nevertheless some special reasons for the appearance in the liquid of such oriented complexes. If the polymerization reaction takes place at the expense of ions or ion-pairs, then the coulombic forces, that lead to the formation of solvate films, could be the source of formation of complexes. Besides, the complexes could be formed with the help of adsorption forces on the walls of the vessel or on the polymer that is forming in the liquid. In the work of Abkin<sup>53</sup> presented to the symposium, very interesting data are adduced on the role of the container wall during radiation-polymerization of styrene in a solution of ethyl chloride at a temperature of -78°. It turned out that the polymerization speed increases with the increase of the ratio s/v, i.e., the ratio of surface to volume of the container, and is extrapolated to zero, when the ratio s/v tends toward zero. This somehow indicates that the reaction takes place in a monomeric layer adsorbed on the wall of the container.

Warral<sup>22</sup> observed a strong increase in polymerization speed for isobutylene at a low temperature, when additional solids were introduced into the container. Medvedev and Kristalnii<sup>23</sup> also observed this effect in the presence of various powders. The effect was the stronger, the finer were the powders (for the same weight), i.e., the greater was the

-26-

surface solid. The effect of speed increase depends little on the chemical nature of powders.

Adler, Ballantine, and others<sup>54</sup> in a lecture presented to this symposium show that the polymerization reaction flows in a liquid on the surface of the polymeric lumps, causing their growth up to formations easily visible by a microscope.

Thus there are certain reasons to assume that polymerization in a liquid is also connected with the formation of correctly oriented groups of monomeric molecules. This, as the author believes, also allows us to further explain the peculiarities of polymerization in these liquids at low temperatures.

Such is the qualitative picture of the simultaneous transition of a whole crystalline monomer to a polymeric chain.

The author hopes that it will be possible in the future to substantiate the presentation set forth, and thus to discover the chemical consequences from the representation of collective levels of monomeric crystals for the chemistry of polymerization processes similarly to the way in which at present their role becomes apparent in explaining certain physical properties of conjugated polymers. We shall talk about this in the following portion of the lecture.

Before passing to the results of the investigations by the EPR method of new polymeric classes, the author reviews the basic types of EPR signals in systems that have previously been thoroughly investigated.

-27-

1. Free radicals with a non-coupled electron localized on a definite atom.

In the majority of cases which interest organic chemists (the radicals containing atoms with nuclear magnetic moments) there arise characteristic EPR spectrum with a hyperfine structure dependent on the interaction of a non-coupled electron with magnetic moments of neighboring nuclei. Below we shall adduce several examples.

(a) In Figure 1 are shown the EPR spectra for hydrogen and deuterium obtained in a frozen solution of ions of divalent iron in acidified water illuminated at  $-196^{\circ}$  by the light of a mercury lamp; the acidified water is enriched with deuterium (Bubnov, Shelimov). As may be seen in the figure, the hydrogen atoms possessing a spin of  $\frac{1}{2}$ , yield two lines of hyperfine structure with a separation of 500 oersteds. The deuterium atom with nuclear spin 1 yields three lines, corresponding to three possible values for the projection of a nuclear spin (-1, 0, +1), with a separation of 78 oersteds from one another. The separations indicated between lines in both cases coincide very nearly with the splitting magnitudes obtained by Rabi in atomic clusters. This points to the absence of any interactions occurring in a solid of H and D atoms with the surrounding environment.

(b) Figure 3 shows the spectrum of a methyl radical obtained during the photolysis of polydimethylsiloxane (Bubnov). The spectrum consists of four lines with identical separations between them (25 oersteds) and with an intensity ratio 1:3:3:1.

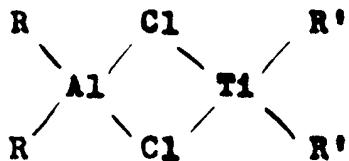
-28-

This spectrum is the result of the interaction of a non-coupled electron of a hydrogen atom with three equivalent protons of the methyl group. Four states corresponding to the various orientations of the spins of the three protons are possible.

$\uparrow\uparrow\uparrow$	a-priori probability 1		
$\uparrow\uparrow\downarrow$	"	"	3
$\uparrow\downarrow\downarrow$	"	"	3
$\downarrow\downarrow\downarrow$	"	"	1

Carbon ( $C^{12}$ ) does not have a nuclear spin.

(c) Upon interaction of aluminum alkyls with halides of titanium, there are formed complexes which catalyze polymerization. If we take the compound  $(C_5H_5)_2TiCl_2$ , then both components and the reaction product are soluble in toluene and benzene. Here the structure of the product, as is shown by X-ray structure data of Natta<sup>24</sup> may be presented by the diagram:



In this compound there must be one non-coupled electron. In connection with this Shilov and others<sup>25,26</sup> at the Institute of Chemical Physics discovered the EPR signal which in the case of bridges of Cl atoms has a poorly solved hyperfine structure.

The substitution of one or both atoms of chlorine for hydrogen leads to the formation of new complexes, whose EPR

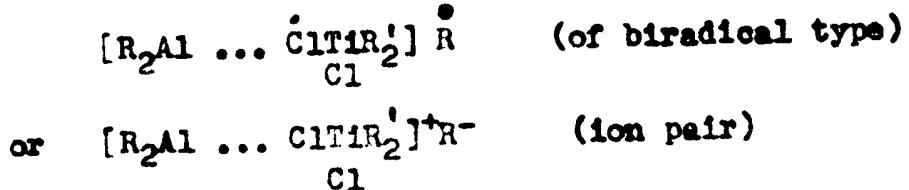
27

spectra have a well solved hyperfine structure (Figure 4). The deciphering of this structure showed that the spin electron density is distributed between aluminum, titanium and two H atoms.

Digressing from the question examined, the author will dwell on the question of the role of complexes (of the Ziegler type) which are catalysts for polymerization.

Natta already found that the blue complex, concerning the structure of which we just spoke, has a weaker catalytic activity.

On the basis of his experiments Shilov came to the conclusion that the intermediate complex which is catalytically active one may represent in a general form as



In greater likelihood the true structure is intermediate between these two. One of the alkyl groups, weakly connected with the remaining part of the complex, possesses certain properties of free radicals (e.g. may disproportionate with another similar particle), but may almost not recombine. Therefore, the reaction of titanium halides with aluminum triethyl takes place almost instantly with the emission of ethane and ethylene, but aluminum trimethyl forms the stable complex shown above. In the reaction with olefins,  $CH_3$  (or  $CH_3^-$ ) in this complex is changed to a larger radical capable of dis-

-30-

proportionating with other  $\text{CH}_3$  groups. Therefore, as was shown by Shilov together with absorption of olefin there occurs the emission of methane and the formation of a blue non-active complex.

Naturally we are faced with the general question whether there are not so-called ion-pairs in certain cases as intermediate formations between ion and biradical structures.

2. Free radicals with delocalized un-coupled electrons, i.e. not fixed to any atoms in a molecule.

Each non-coupled electron with sufficient exchange frequency is in an identical average field of nuclear spins. As was shown by Anderson, one obtains here a narrow single line of paramagnetic resonance, corresponding to the average (zeroth) value of the magnetic field of the nuclear spins.

(a) Figure 5b shows the EPR spectrum of a free radical of diphenylpicrylhydrazyl, dissolved in benzene. The spectrum has a typical hyperfine structure (on account of interaction with nitrogen nuclei). The general width of the spectrum is  $\sim 50$  oersteds. In a solid state, when the molecules are replaced by uncoupled electrons with sufficient frequency (collective level), the spectrum represents a single narrow line (Figure 5a).

(b) Figure 6 shows the EPR spectrum of a guanylic acid-monomer, which is one of the components of complex biopolymeric nucleic acids, after exposure to gamma rays. As may be seen, the spectrum consists of a series of lines of hyperfine structure with a general width of about 100 oersteds. In a polymer,

-31-

ribonucleic acid, in which uncoupled electrons, arising upon exposure to gamma-rays, are delocalized, one observes a narrow (8-9 Geraseds) EPR line without hyperfine structure (Figure 7) (Blumenfeld's data).

3. Uncoupled electrons with strong collective interaction.

In this case one observes an unusually strong widening of the EPR signal (hundreds and thousands of Geraseds) and an asymmetry of these wide lines. Two types are widely known:

(a) Metals with good electrical conductivity, where the intensity of the signal is small.

(b) Ferromagnetics and anti-ferromagnetics, where powerful internal magnetic fields are formed that lead to a very great signal intensity. Figure 8 shows the EPR spectrum of a typical  $\text{Cr}_2\text{O}_3$  anti-ferromagnetic.

Terminating here the short description of the classification of EPR signals, the author passes directly on to the subject of the second part of the lecture.

During 1959 there were discovered through the EPR method new magnetic effects in organic structures; these effects are connected with the appearance of narrow and wide EPR lines. Let us begin with the problem of narrow lines. Back in 1948 Kozyrev<sup>27</sup> in Kazan discovered in carbohydrates (in the solid phase) with conjugate double bonds, a narrow EPR signal, in which the intensity of the signal increased with the increase of the length of the conjugate chain. Experiments were conducted at one (room) temperature. Kozyrev obviously wrongly

-31-

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-32-

interpreted this phenomenon as a result of excitation to a triplet (biradical) state, which with the increase of conjugation approaches the ground state to such a degree that it becomes noticeably populated even at room temperature. Subsequently, various foreign and Soviet authors obtained analogous results in various conjugate systems. In the middle of 1959 there appeared the work of Matsunaga<sup>28</sup>, who had proven that in the case of conjugated <sup>hydrocarbon</sup> carboxylate-dinaphthoquinone, the narrow EPR signal observed in a crystalline state increases at lowered temperature <sup>in</sup> its intensity according to Curie's law; this, obviously, excludes the interpretation of the effect as a result of excitation to a triplet state. Matsunaga supposes, however, that in a solution a very small portion of molecules forms bimolecular complexes with sharply lowered (considerably less than  $kT$ ) energy of excitation to a triplet state. In a solid they do <sup>in</sup> freeze and give the observed signals. Let us observe that in a solution the signal disappears.

At the Mendeleev Congress in March 1959, the author in the summary lecture<sup>29</sup> reported in particular very briefly that narrow EPR lines, according to Blumenfeld's and Berlin's experiments<sup>30,31</sup>, arise in conjugated polymeric systems. Similar articles of these authors appeared in the second half of 1959. First of all the presence of narrow signals was shown in polyphenylacetylene, and later on also in other conjugate polymeric systems (polyphenylene, the polymer of tetracyanoethylene, polyphthalocyanine, polyaminoquinone). In a solution of polymeric molecules the signals remain.

-33-

In September 1959 there was published the article of Topechiev, Kargin, Krensel, Polak, Devyдов and others<sup>32</sup>, who had discovered narrow EPR signals in thermally processed polyacrylonitriles.

Blumenfeld and Berlin showed that

1. The intensity of the signal does not depend on the means of obtaining the polymer, but is determined by the length of conjugated chain and is preserved in a solution down to the highest dilutions (Figure 9), i. e. it is a property of the polymeric molecule, and not of the structure of the solid polymer as a whole. These data exclude the hypothesis of Matsumaga in any cases applied to these polymeric compounds.

2. The temperature rate rigidly follows Curie's law in the interval from +150 to -196°, i.e. paramagnetic signals are not a result of thermal excitation to a triplet state.

Voyevodskii and Tikhomirova<sup>33</sup> showed that the narrow signals in the coals also depend on a system of conjugated bonds of condensed aromatic in the lattice of coals, and do not indicate the presence of genuine free radicals, as was believed before. Thus, in 1959, a new effect characteristic of conjugate systems actually was found; this effect appeared especially strongly in conjugated chains of macromolecules.

The appearance of a narrow signal may be analyzed as an indication of a degree of non-coupled state of electrons in conjugated systems. Knowing the intensity of a signal and of the absorption calculated for one non-coupled electron

(under given observation conditions), one may determine the degree of uncoupling, i.e. the number of non-coupled electrons ~~per gram~~ <sup>per gram</sup>, consequently, for one molecule. For monomeric conjugated systems the number of non-coupled electrons calculated per molecule was a small fraction ( $10^{-4} - 2.5 \times 10^{-3}$ ), and for dissolved conjugated polymers it was not higher than 1/5. Inasmuch as the degree of uncoupling is a fractional number, obviously it is impossible to speak of any isolated uncoupled electron, but only ~~for~~ <sup>of</sup> the degree of uncoupling of the electron cloud as a whole. The fractional value of uncoupling in a molecule, obviously, cannot be explained by the fact that in one of the molecules there is one uncoupled electron, and in others there is no uncoupling at all, since all molecules in a solution are, of course, identical.

From all that has been said above, it obviously follows that the degree of uncoupling is not connected with the excited, but with the basic state of the molecule. There still is no theoretical explanation of this effect.

Let us pass on to the analysis of magnetic effects connected with the appearance of wide EPR lines.

In the beginning of 1959 there was published an article of Blumenfeld, Kalmanson and of a Chinese M.A. candidate Shen-Pei-gen<sup>34</sup>, who discovered new magnetic properties for nucleic acids and their complexes with proteins. They discovered extremely wide (700-1000 oersted) asymmetric lines of magnetic resonance of large integral intensity for native nucleic acids and nucleoproteins. Figure 10 shows a typical EPR spectrum of native deoxyribonucleic acid.

As regards to the concentration of uncoupled electrons, considering that these compounds are ordinary paramagnetic substances, we obtain huge values ( $10^{21}$ - $10^{22}$  uncoupled electrons per gram). However, the width, shape and temperature dependence of these lines differ from the corresponding characteristic paramagnetic materials. In the laboratory of Blumenfeld<sup>35</sup> were studied in detail these completely unexpected magnetic properties of biopolymers, which according to formerly existing ideas should be diamagnetic. It was discovered that these compounds are characterized by a positive static magnetic susceptibility, which decreases according to a hyperbolic law when the intensity of the magnetic field is increased. Thus we observe a clear saturation effect characteristic of ferromagnetics. At the same time, in contrast to all known ferromagnetics, there is no residual magnetic moment when the external magnetic field is switched off. The behavior of these signals when the temperature is lowered recalls the change in EPR spectra of compounds of the type  $\text{Cr}_2\text{O}_3$ ,  $\text{MnO}$  and of other typical antiferromagnetics. On the other hand, the saturation in relatively small fields recalls the ferromagnetics. Obviously a new class of magnetic phenomena has been discovered, which does not fit into the accepted classification. Let us note that Bothner-By, Balass, and Gergely<sup>36</sup> reported at the IVth International Biochemical Congress at the end of 1958 that their data bear witness to the presence of strong internal magnetic fields in deoxyribonucleic acids.

-36-

It is clear from all available experimental material that there is a collective phenomenon dependent on the existence of isolated regions (singular domains), inside of which uncoupled electrons strongly interact. The appearance of effects obtained by Blumenfeld is closely linked to the preservation of the well-regulated structure of the biopolymer. When the structure is destroyed (e.g. in thermal denaturation) the effects disappear; in the case of additional structure (e.g. when compounds with proteins are formed) the effects increase. Analogous specific magnetic properties were discovered in this laboratory for native tissues containing nucleic acids (Kalmanson), for natural nucleoproteins (Kulibakin), for growing bacterial cultures (Samoylov). At present Blumenfeld is working out a theory of these singular magnetic phenomena. From this theory it follows that in the structures indicated one may expect the appearances of very great values for electric polarization in comparatively weak electric fields.

An analogous original "pseudo-ferromagnetism" was also discovered in many polymers with coupled double bonds, containing, as a rule, a heteroatom or atoms of a metal in the chain of conjugation, and also electron-donor or electron-acceptor groups<sup>31,37</sup>. These new polymers were synthesized in Berlin's laboratory. As in the case of all polymers with coupled double bonds, these polymers give narrow EPR lines of the type described above. However, in the given case, in a solid state this narrow signal is superposed on a

wide line of huge integral intensity. Just as in the case of nucleic acids, the appearance of a wide signal is accompanied by a positive static magnetic susceptibility, which shows a clear saturation. Upon dissolving a polymer the wide line and the positive magnetic susceptibility disappear, and the narrow signal remains. Thus the wide line characterizes the structure of a solid polymer as a whole, although its appearance depends also on the properties of isolated polymeric molecules. Analogous magnetic properties (wide EPR lines) were discovered in the laboratory of Blumenfeld for certain crystalline monomers with a sufficiently branched system of conjugate bands (certain dyes, oxyderivatives of organic condensed hydrocarbons). As in the case of polymers, these effects disappear upon dissolving.

Thus, the wide EPR signal in synthetic polymers appears:

1. In the presence of a narrow signal, characterized by delocalization of an electron in the individual molecule;
2. In the presence of sufficient well-organized sectors of crystalline structure.

In other words, a collective assembly of correctly disposed coupled polymeric molecules forms a spatial region ("domain") with collectivization of electrons over this entire volume. In this connection there arises another higher degree of collectivization with an increase of the degree of uncoupling of electrons, and of their strong interaction; the latter gives rise to the magnetic properties of the crystals. Let us remember that there is here an analogy with behavior of

-33-

certain coupled monomers, which do not yield collective effects in a solution, i.e. they exist in the form of isolated molecules and, nevertheless, yield narrow lines of delocalized electrons in a crystalline state. Let us note that this to a certain degree substantiates the previously expressed supposition about the presence of general electron levels for the system of regularly disposed crystalline monomers, although the latter may only have one double bond.

All of the above described new magnetic properties of these polymeric systems bear witness to the existence either of collective levels, on which the electrons are delocalized throughout the entire system (narrow EPR lines), or of regions with a strong interacting cloud of collectivized electrons (wide EPR lines).

Thus in the light of new data, isolated macromolecules and sometimes also well ordered aggregates of macromolecules must be considered from the viewpoint of their electron structure as a single complete system. Undoubtedly such peculiarities of electron structure must strongly influence the physical and chemical properties of similar substances.

Besides the magnetic properties, electrical properties constitute another important physical property. In this connection, of course, the electrical conductivity is determined by the state of the specimen as a whole, and not merely by the structure of isolated molecules. As was shown, in conjugated systems of both types (narrow and wide signals), there are general levels and, of course, in the conjugated

-39-

molecule itself, and also in the domains, there is practically no resistance to the movement of electrons or of "holes" under the action of an external electric field. The resistance arises only upon transition of the electron from one polymeric molecule to another or from one domain to another. Inasmuch as the volume of the domain is considerably larger than that of the polymeric molecule, one may expect for these systems considerably larger values of electric conductivity. It has really been known for a long time that polynuclear aromatic hydrocarbons forming good molecular crystals possess at room temperature a greater electrical conductivity than that of other organic compounds. As Blumenfeld shows, for some compounds of this type a wide EPR signal was found.

Talroze, Frankevich and Balabanov<sup>38</sup> at the Institute of Chemical Physics of the Soviet Academy of Sciences measured the electric conductivities of a large number of above enumerated new polymers synthesized in the laboratory of Berlin (Parin, Cherkashin and others). In this connection, it turned out that increased electric conductivity at room temperature is observed as a rule for the same specimens which yield wide EPR signals. On the other hand, the authors drew attention to the fact that the specimens of polymers with continuous chain of conjugation, which yield narrow EPR lines and do not reveal increased electrical conductivity at room temperature, possess in many cases a very great (up to 50 Kcal/mole) energy of activa-

-14-

tion of electric conductivity; in this connection the law of Arrhenius ( $\sigma = \sigma_0 e^{-E/RT}$ ) is observed with great exactness. Talroze analyzed the dependence between "activation energy" and the pre-exponential term  $\sigma_0$  for polymers (studied by him) with narrow and wide EPR signals, and also for different organic compounds, previously known, including polynuclear aromatic compounds. The results of this study are shown on Figure 11. Along the abscissae the logarithm of the pre-exponent  $\log \sigma_0$  is plotted, and along the ordinates the activation energy  $E$  is given. Simultaneously, for a large number of specimens studied by the EPR method by Blumenfeld, there is indicated the presence of a narrow ( $\square$ ) or wide ( $\circ$ ) EPR line, and also the absence of EPR signal altogether ( $\triangle$ ). The points ( $\nabla$ ) belong to the specimens for which there still are no data concerning EPR signals. It turned out that there is a very clear symbate between the change of energy of activation and of the pre-exponential term among the specimens. It is especially interesting that a fairly good linear dependence between  $\log \sigma_0$  and  $E$  encompasses practically all specimens, for which no wide EPR lines are observed. However, the specimens with wide EPR lines are considerably "displaced" from a straight line on Figure 11 in the direction of large values of electric conductivity at room temperature<sup>39</sup>.

In this connection the magnitudes of electrical conductivity, which scientists of various countries were already able to obtain for polymeric materials, are very considerable.

-41-

Thus Topchiev, Kargin, Krenzel, Polak, Davydov and associates<sup>55,32</sup> in the USSR were able to obtain after thermal processing of polyacrylonitrile a substance with an electrical conductivity of  $10^{-3} \text{ ohm}^{-1} \text{ cm}^{-1}$  at a temperature of  $20^\circ$ . A little later by analogous means Pohl<sup>40</sup> (USA) obtained specimens with an electric conductivity of the same order. Epstein and Wild<sup>41</sup> in the USA obtained specimens of polyphthalocyanine-copper with  $\sigma = 2.5 \times 10^{-2} \text{ ohm}^{-1} \text{ cm}^{-1}$  at a temperature of  $25^\circ$ . Neill and Weiss<sup>42</sup> in Australia obtained polyxanthene with  $\sigma \approx 10^{-4} \text{ ohm}^{-1} \text{ cm}^{-1}$  at a temperature of  $25^\circ$ . The electrical conductivity of a polymeric chelate compound of tetracyanoethylene with copper, synthesized in the Institute of Chemical Physics in the laboratory of Berlin and studied at the Institute of Electrochemistry of the Soviet Academy of Sciences of Frumkin by Burshtein with associates<sup>43</sup> amounts to  $5 \times 10^{-6} \text{ ohm}^{-1} \text{ cm}^{-1}$  at  $20^\circ$ . The electrical conductivity of polyphenylamine synthesized in the same laboratory and studied at the Institute of Chemical Physics is equal to  $10^{-6} \text{ ohm}^{-1} \text{ cm}^{-1}$  at  $25^\circ$ . In all cases higher values were observed for the dielectric constant.

It is interesting to note that the specimens, to which the points correspond on the right upper part of the straight line in Figure 11, and which possess very large values of  $\sigma$  and  $\kappa$ , upon heating, naturally increase very rapidly in electrical conductivity. Thus, for instance, the electrical conductivity of specimens of molecular complexes of

-42-

acenaphthene and of chloranil, obtained by Parini in Berlin's laboratory at a temperature of  $25^{\circ}$  is equal to  $10^{-15}$  ohm $^{-1}$  cm $^{-1}$ , and at  $65^{\circ}$  reaches  $10^{-7}$  ohm $^{-1}$  cm $^{-1}$ , but at high temperatures these specimens are destroyed. The connection obtained between  $\mathbb{C}$  and  $\mathbb{E}$  has many kinetic analogues, especially with processes in solids, in particular in catalysis. There does not exist a full understanding of this so-called compensationary effect; recently Roginsky and Khait<sup>44</sup> in the USSR have put forward certain theoretical bases for this effect. However, one must emphasize that for suitable scales - upon change of the pre-exponential term of the order of 60, this effect was never observed.

Talroze<sup>45</sup> supposes that the presence of a linear relation, encompassing all substances without wide EPR lines and simultaneously possessing a small electrical conductivity at room temperature, and a sharp deviation from this dependence of specimens with high electrical conductivity (and simultaneously with wide EPR lines) will in the future possibly become the basis for a classification that distinguishes substances with strong collective interaction and correspondingly great electric conductivity from substances with small collective interaction and correspondingly poor conductors of electricity at ordinary temperatures. In conclusion, I would like to note that the polymeric systems surveyed above, which give an EPR spectrum, possess, as was shown by preliminary experiments (Institute for Elemental Organic Compounds, Institute of Petrochemical Synthesis,

-43-

Institute of Chemical Physics), catalytic properties in certain oxidizing and reducing reactions<sup>59</sup>.

The report given consists of two rather characteristically different parts. The first part is devoted to the polymerization at low temperatures, and the second to physical properties of new classes of polymers. However, both these parts are connected in some measure by one general idea, which consists of the recognition of the important role of the collectivization of electrons and of their energy levels both in polymerization processes and in physical properties. The role of such concepts will probably prove especially important in the future for the understanding of biochemical processes.

Figure Captions

Fig. 1. Dependence of  $k_g$  on  $1/T$  for methyl methacrylate

Fig. 2. EPR spectrum for H and D atoms

Fig. 3. EPR spectrum for methyl radical

Fig. 4. EPR spectrum corresponding to the complex

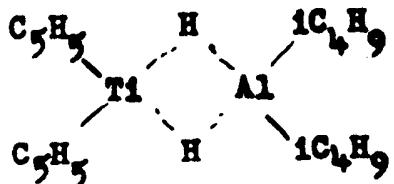


Fig. 5. EPR spectrum of diphenylpicrylhydrazyl

a. in a solid state

b. in a solution of C<sub>6</sub>H<sub>6</sub>

Fig. 6. EPR spectrum of guanylic acid after exposure to gamma-rays

Fig. 7. EPR spectrum of ribonucleic acid

Fig. 8. EPR spectrum of Cr<sub>2</sub>O<sub>3</sub>

Fig. 9. EPR spectrum of polyphenylacetylene

a. in solid state

b. the same quantity in a benzene solution

c. the same as in b, but diluted 5 times

Fig. 10. EPR spectrum of deoxyribonucleic acid (DNA)